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COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 707

October 7, 1953

Report No. Q-7
(Quarterly Summary)

SUBJECT: CSR Nitropolymer Research

CONTRACT: Nonr-1205(00)

PERIOD COVERED: July 1, 1953 to September 30, 1953

WRITTEN BY:

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Jerome Martin
Director of Research

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CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr-1205(00).

I. SUMMARY

A. This quarterly report is the first under Contract Nonr-1205(00) and covers the period from July 1, 1953 to September 30, 1953. The object of the contract is: 1. Conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the applications of processes not now employed in the preparations. 2. Conduct investigation of the process and prepare a pilot lot of 2,2-dinitropropyl acrylate polymer, not to exceed 1,000 lbs.

B. The more important results and conclusions of the work are presented below.

1. There has been prepared in the pilot plant 1,178 lbs. of 2,2-dinitropropanol.

2. Polymers prepared in the laboratory from each pilot plant batch of 2,2-dinitropropanol have been acceptable as based on solubility and relative viscosity.

II. TECHNICAL PROGRESS

A. INTRODUCTION

The principal effort during the quarter has been concentrated on the production of not more than 1,000 lbs. of 2,2-dinitropropyl acrylate polymer. During this report period, we have prepared 1,178 lbs. of 2,2-dinitropropanol from purified nitroethane by means of the Shechter-Kaplan reaction, and are now ready to proceed with the preparation of the monomer and its subsequent polymerization.

B. NITROETHANE PURIFICATION

Commercial nitroethane was purified by rectification in a 40-plate, pilot plant column. To remove the head cut, a 25 to 1 reflux ratio was used; for the center cut, a 10 to 1 ratio; and for the tails, a 25 to 1 ratio was again used. Mass spectrograph analysis of cuts used are shown in Table 1 and indicates the low concentration of nitromethane obtained as desired.

Table 1

ANALYSIS OF NITROETHANE CUTS USED IN 2,2-DINITROPROPANOL PRODUCTION

Run	Cut	Pounds	% Nitromethane	% Nitroethane	% Nitropropane
311	4	200	0.04	98.86	1.09
311	5	300	0.00	98.73	1.27
311	6	65	0.00	98.30	1.69
311	6A	157	0.00	98.19	1.86
311	7	165	0.00	97.63	2.37
313	4	100	0.08	99.48	0.40
313	5	100	0.01	99.93	0.65
313	6	100	0.00	99.42	0.53
313	7	86	0.00	98.91	1.07
		Weighted Mean	0.01	98.60	1.28

C. PREPARATION OF DINITROPROPANOL

1. Discussion

The dinitropropanol was prepared in the pilot plant in 1.0 lb. mole runs, using the purified nitroethane in the Shechter-Kaplan reaction. The loss of silver nitrate is much higher than anticipated with no explanation offered as to point of loss or reason for the loss. In an effort to account for some loss, the raffinate, after extraction of the product, was made basic and worked up to recover any silver nitrate which had passed through the reaction. The recovery was small, less than 1% per run.

There was considerable difficulty in isolating solid product from the concentrated extract. If a vacuum of 20 mm. of mercury or better was not obtained in the final concentration, very little solid would separate on cooling the concentrate. If the concentrate was stripped exceedingly well, the material set up to such a high solid content that centrifuging was very difficult. And, if the relative humidity of the air was over 50%, there was considerable loss of solid product from the centrifuge by hydroscopicity.

The yield of solid product was 49.2% which is quite low compared to the reported mean yield of 74.1% in Table 2. The yields in Table 2 were determined by concentrating samples of the extract in the laboratory and weighing the solid residue obtained.

It is interesting that crops 3, 4, 5, and 6 seem to be as high in quality for polymerization purposes as the first and second crops as is shown by Table 3.

Table 2

SUMMARY OF PILOT PLANT 2,2-DINITROPROPANOL RUNS

Batch	Recovery of Silver Nitrate	Yield by Lab Conc.		Crops				
			1	2	3	4	5	6
3	87.9%	67.4%						
4	84.0	72.7						
5	94.3	76.0	380 lb.					
6	98.7	n.s.						
7	90.2	73.4						
8	100.0	n.s.						
9	96.8	n.s.	156					
10	93.3	n.s.		133				
11	88.0	72.0		175	84	46	21	6.5
12	95.7	56.7	41					
13	93.8	66.7						
14	92.1	81.5						
15	95.4	84.5	135.5					
16	90.8	80.7						
Mean	92.9%	74.1%						

Total solid: 1,178 lb.
49.2%

Table 3

2,2-DINITROPROPYL ACRYLATE MONOMER AND POLYMER FROM PILOT PLANT 2,2-DINITROPROPANOL

Batch	Monomer Yield	Crude Polymer N %	Polymer Yield	Washed, Dried Polymer N %
5,6,7 (6-68)		3.72		
3,4,5,6,7 (6-74)	81%	4.07	67%	6.11
3,4,5,6,7 (6-71)	85	2.74	70	3.62
8,9,10 (6-70)	64	3.74	55	2.78
8,9,10 (6-72)	69	3.32	70	4.16*
11,12,13 (6-75)	75	3.16	62	4.86
2nd crop (6-79)	95	2.74	74	
2nd crop (6-76)	93	2.74	82	
3rd crop (6-77)	92	2.68	84	
4th crop (6-80)	91	2.28	66	

*Analysis: No trace of Cl
Calc'd. for N: 13.72%
Found: 13.98

2. Procedure

Salt Solution Preparation: The reaction vessel used in this preparation is equipped with an efficient stirrer and cooling coil. To 276 lb. of condensate water and 76.1 lb. of fractionated nitroethane is added 88.0 lb. of 50% sodium hydroxide solution. When the nitroethane is all in solution as the sodium salt and the temperature is down to 20°C., 83.5 lb. of 36% formaldehyde solution is added at such a rate as to keep the temperature below 20°C. After the formaldehyde solution is all in and the reaction stirred for 1/2 hr., 187 lb. of 40% sodium nitrite solution is added and the solution is ready for the reaction.

Silver Nitrate Solution Preparation: A reaction vessel is used which can be heated and cooled, and contains an agitator. To the recovered filter cake from the previous run in the reaction vessel is added 280 lb. of 60% nitric acid in portions. When the reaction has subsided it is agitated, then slowly heated to about 90°C. After an hour or two at this temperature a check is made to see if the solution is still acidic and the solids all in solution. When the reaction is complete, the solution is cooled, pH adjusted to about 5, and the total weight of solution made up to 800 lbs. with condensate water. A sample is titrated with standard ammonium thiocyanate solution and the silver nitrate concentration brought to 340.0 lb. by adding the required amount of silver nitrate crystals. The pH is finally adjusted to 5.9 ± 0.2 and the solution is ready for the reaction.

Reaction: To the silver nitrate solution is added the salt solution in the shortest possible time, about 15 min., and the resulting slurry stirred for 1/2 hr. During the reaction, the temperature momentarily rises to about 30°C. but is rapidly brought back to cooling water temperature. The slurry is filtered in a 50-gal. filter crock and the precipitate is washed well with water.

Extraction: The filtrate and washings from the above reaction are pumped to a decanter containing the second extract from the previous run. After agitating and separating, this extract is concentrated at 300 mm. mercury pressure to remove solvent. The raffinate is extracted a second time with 560 lb. of ethyl acetate and the extract held for the succeeding batch. The raffinate is made basic with caustic and held for possible recovery of additional silver.

Isolation: The stripped concentrate from the extraction is treated with carbon and combined with two similar batches. These combined batches are then stripped of all volatile material at 20 mm. of mercury pressure or less at 70 to 80°C. This final concentrate is cooled and centrifuged to obtain a first crop of about 150 to 200 lb. (33 to 45%). Second and third crops of good, solid dinitropropanol are obtained by working up the centrifugate to obtain a total solid yield of about 220 lb. (49%).

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